

ELECTRODEPOSITION OF THE ALKALI METALS  
FROM PROPYLENE CARBONATE

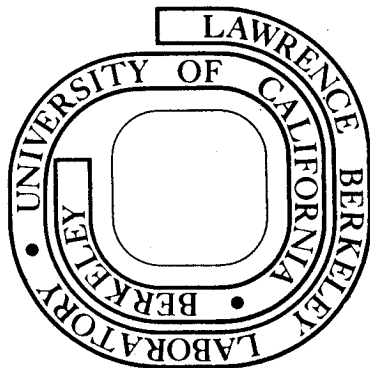
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# Electrodeposition of the alkali metals from propylene carbonate

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The alkali metals were electrodeposited from various solutions in propylene carbonate (PC). Li, Na, K, Rb and Cs were electrodeposited from solutions of their chlorides and  $\text{AlCl}_3$  in propylene carbonate (PC) at ambient temperature. In addition, lithium was deposited from  $\text{LiCl}$ ,  $\text{LiBr}$ ,  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ , and  $\text{LiBF}_4$  solutions in PC. Sodium was reduced from  $\text{NaClO}_4$ ,  $\text{NaPF}_6$ , and  $\text{NaBF}_4$  solutions. Potassium was obtained from  $\text{KPF}_6$  solution.

A new process is proposed for the production and electrorefining of the alkali metals at ambient temperature. Alkali metal amalgam from the commercial mercury-chlorine cell is transferred into an  $\text{AlCl}_3$ -PC electrorefining cell, where the alkali metal is dissolved anodically from the amalgam, and deposited in a pure form at the cathode.

## 1. Introduction and general background

Electrodeposition of metals from aqueous solution is restricted primarily by thermodynamic limitations. Metals which have significantly higher electrode potentials than hydrogen cannot be deposited from aqueous solution; the solvent is decomposed instead, resulting in hydrogen evolution. The alkali metals are the most reactive and cannot be deposited in solid form from aqueous solution; they react violently with water. Alkaline earth metals and most of the transition metals also cannot be electrodeposited from their aqueous solutions. The use of nonaqueous solvents has been recognized for many years [1, 2], and the search for the 'magic' solvent that would permit a wider range of potentials for oxidation or reduction, led to the development of a wide and promising field-electrochemistry in nonaqueous solvents.

The search for an alternative to water as a solvent was started in the beginning of the century by Walden [3]. An early review on the deposition of metals from various nonaqueous solvents was presented by Audrieth and Nelson [4], and later by

Audrieth and Kleinberg [1]. Brenner [5] reviewed the deposition of metals from organic solvents up to 1964. Most of the work in this field was unsystematic and covered only the most familiar organic solvents, in particular, pyridine, formamide, acetamide, acetonitrile, and various alcohols. Butler [8] reviews the electrochemical behaviour of the alkali metal electrodes in nonaqueous aprotic solvents.

Of all the classes of solvents, aprotic solvents proved to be the most promising. These solvents have high dielectric constants (greater than 30), have weak acidic and basic character, and are difficult to oxidize or reduce.

The present work concentrates on the exploration of the electroreduction of the alkali metals at ambient temperature from their solutions in propylene carbonate. The goal was to develop a new process for the electrorefining and separation of the alkali metals at ambient temperature [9] as an alternative to the high temperature molten salt processes by which these metals are currently produced.

Propylene carbonate (PC), originally proposed for electrochemical applications by Harris and

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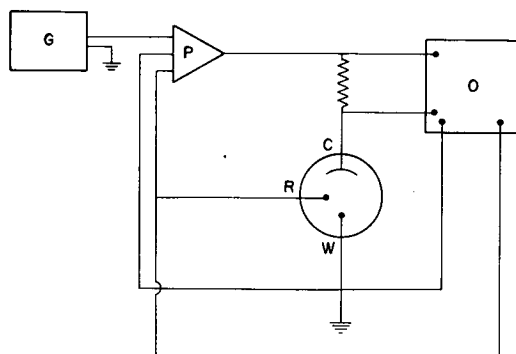


Fig. 1. Apparatus for cyclic polarization. C – counter electrode; G – wave form generator; O – oscilloscope, or x-y recorder; P – potentiostat; R – reference electrode; W – working electrode.

Tobias [6], is a member of a group of cyclic esters. PC is a dipolar aprotic solvent with high dielectric constant (65 at 25°C), low melting (–49°C) and high boiling (241°C) points, and dissolves many inorganic salts. The decomposition potential of PC is above 4 V [7]. The electrochemistry and application of PC was reviewed by Jasinski [7].

## 2. Experimental

### 2.1. Solvent purification

Propylene carbonate (Jefferson Chemical Company, Houston, Texas) was distilled at 0.5 mm Hg in a commercially available vacuum distillation column (Semi-CAL series 3650, Podbielniak, Franklin Park, Illinois) packed with stainless steel helices. The reflux ratio was 60–100 and the head temperature 65°C. The first 10 and the last 25% of the solvent were discarded. The receiver system of the column was rebuilt with glass drip tips and needle valve stopcocks (Delmar Scientific Laboratories, Inc., Maywood, Illinois) equipped with teflon 'O' rings. Argon gas was bubbled through the solvent during distillation. The collection vessel was not detached from the column; the solvent was discharged directly into the dispensing vessel. The transfer was done under an argon atmosphere. The dispensing vessel was evacuated on the vacuum line to approximately 50  $\mu$ m Hg, closed tightly and transferred into the glove box.

The 'as received' solvent contains a few tenths of a percent of the following impurities: water, propylene glycol, propion aldehyde, propylene

oxide [7]. Gas Chromatographic analysis of the product performed in this laboratory showed the water content to be always below 50 ppm [10]. The presence of a second impurity at a very low concentration was identified as propylene oxide, and its concentration was estimated below 1 ppm. The Varian Aerograph Model 202A gas chromatograph used for the analysis was equipped with thermal conductivity cells (W filaments) and a 2 ft (0.25 in diameter) column containing 'Poropak Q' (80–100 mesh). The carrier gas was helium. The column, injector and detector temperatures were 110, 140 and 200°C, respectively. The final solutions were treated with molecular sieves (Linde 4A) in order to remove traces of water introduced by the salts. No further analysis was made to check the possibility of cation exchange with the molecular sieves.

Electrodeposition experiments were conducted in an H type cell, the two compartments being separated by a fritted glass. The anode and the cathode were made of platinum foils attached to platinum wires, and were immersed in the solution. The area of the electrodes was approximately 1 cm<sup>2</sup>. Constant current was applied, and the cathode was observed for the nature of the deposit. The solution was stirred during the experiment by a small magnetic stirrer. Deposits were analyzed by X-ray diffraction (Cu K $\alpha$  radiation of 1.540 50 Å, Picker X-Ray, Model 3488K). In addition, the alkali metals were identified using flame spectroscopy.

The experiments were qualitative in nature and were conducted with the purpose of screening possible electrolytes. All electrodeposition experiments were conducted inside the glove box under a dry argon atmosphere. A constant current power supply (Model C 612 Electronic Measurements) was used, and the applied potential was measured by an Electrometer (Keithly Model 601).

### 2.2. Cyclic polarization measurements

The reversible behaviour of the alkali metals and their amalgams in PC solutions was tested by the cyclic polarization technique, in which the potential between the working and the reference electrodes was scanned linearly around the equilibrium potential, both in the cathodic and anodic directions. The solutions were stirred during the

experiments by a small magnetic stirrer. A block diagram of the experimental apparatus is shown in Fig. 1. A triangular potential waveform was generated by a waveform generator, Exact Model 100, connected to a Wenking potentiostat. The current was recorded versus the scanned potential on an oscilloscope (Tektronix) or on a fast X-Y recorder (Autocraft X-Y Recorder, Mosley). The working and the reference electrodes were identical in most cases, except when the working electrode was made of a clean platinum foil.

### 2.3. Electrodeposition in a rotating disk system

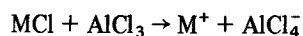
The electrodeposition at relatively high current densities was investigated using a rotating disk system, especially designed for inert atmosphere operation [11]. The disks were made of teflon, and the central electrodes were platinum, stainless steel or nickel. The area of the electrode was about 0.1 cm<sup>2</sup>, and the rotation speed was varied from 0–3600 rpm. Deposition experiments were conducted under a stream of dry argon with the rotating disk serving as the cathode, and an amalgam of the particular alkali metal serving as the anode. A reference electrode was placed in a separate cell connected to the main cell by a small capillary. The tip of the capillary was in the plane of the disk, at 2.4 cm from the centre. The reference electrode was either the corresponding alkali metal, or an amalgam of identical composition to the counter electrode. A Wenking potentiostat served to maintain constant potentials between the working and the reference electrode; the resulting currents were read from the potentiostat dial. Currents were varied up to 5 mA, corresponding to a current density of 50 mA cm<sup>-2</sup>, a practical rate for a commercial electrolysis process. The ohmic drop was excluded from the total overpotential by a current interrupter technique; the immediate drop in the potential was attributed to the ohmic resistance of the solution between the working electrode and the tip of the reference electrode capillary. Rectangular wave form pulses were derived from an E. M. Test Pulser, Lawrence Berkeley Laboratory. The potentials were observed on a Tektronix Oscilloscope operating at 0.01–1.0 ms cm<sup>-1</sup> and 50–200 mV cm<sup>-1</sup>. The ohmic drop was determined at four different currents for each cell, both in the anodic

and cathodic directions. The ohmic resistances were of the order of 300 Ω. The ohmic drop was also calculated according to the method of Newman and Hsueh [12, 13] using experimentally determined values of the specific conductivities of the solutions. The general agreement between calculated and experimentally obtained ohmic drops indicated that the resistances of the electrodeposited metals were quite low.

### 3. Results and Discussion

The search for electrolytic solutions that would enable the deposition of the alkali metals started with a qualitative stage, in which the common alkali metal salts were tested for solubility, and the feasibility of deposition. High solubility is required in order to obtain a low ohmic drop and low concentration overpotential. It appears that a solubility of the order of 1 mol l<sup>-1</sup> is necessary. This concentration corresponds to a specific conductance of approximately 10<sup>-2</sup> Ω<sup>-1</sup> cm<sup>-1</sup>, and permits a relatively wide range operation below the limiting current. The following anions were tested: chlorides, bromides, iodides, perchlorates, hexafluorophosphates, tetrafluoroborates and tetrachloroaluminates. Solubility measurements revealed that all the chlorides, except LiCl, are quite insoluble. Of the bromides, only LiBr and NaBr are moderately soluble. The iodides of rubidium and cesium are insoluble. The perchlorate series revealed that only lithium and sodium perchlorate are highly soluble. Of the tetrafluoroborates, only LiBF<sub>4</sub> and NaBF<sub>4</sub> are soluble. From the hexafluorophosphates, LiPF<sub>6</sub>, NaPF<sub>6</sub> and KPF<sub>6</sub> are soluble. It is not clear whether RbPF<sub>6</sub> and CsPF<sub>6</sub> are soluble as well.

The only common anion which yielded high solubilities for the entire alkali metal series was the chloride-aluminium trichloride complex:



where M is any alkali metal. It was found that in the presence of AlCl<sub>3</sub>, which itself is highly soluble in PC (above 3 mol l<sup>-1</sup>), the solubilities of the alkali metal chlorides rise to a 1 : 1 ratio, except for NaCl. The solubility of NaCl is approximately 0.5 mol l<sup>-1</sup> in the presence of AlCl<sub>3</sub> (1 mol l<sup>-1</sup>) in PC (1 : 2 ratio).

The following results were observed:

### 3.1. Lithium

**3.1.1.  $\text{LiCl}$ .** The solubility of  $\text{LiCl}$  in PC is below  $0.1 \text{ mol l}^{-1}$ ; ( $4.0 \cdot 10^{-2} \text{ mol l}^{-1}$  was reported by Butler *et al.* [14]). Li was deposited from the saturated solution; the applied potential was very high because of the low conductance.

**3.1.2.  $\text{LiBr}$ .** The solubility of  $\text{LiBr}$  in PC is  $2.43 \text{ mol l}^{-1}$  [15]. The metal was deposited from a  $1 \text{ mol l}^{-1}$  solution of  $\text{LiBr}$  in PC at a current density of  $1 \text{ mA cm}^{-2}$ . The lithium deposit was grey and formed a Li-Pt alloy with the platinum cathode. The alloy was similar to the one obtained during the electrodeposition from a  $\text{LiClO}_4$  solution in PC.

**3.1.3.  $\text{LiClO}_4$ .**  $\text{LiClO}_4$  was found to be the best lithium electrolyte in PC. The solubility of  $\text{LiClO}_4$  in PC is  $2.1 \text{ mol l}^{-1}$  [16], and the conductivity is relatively high,  $5.6 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ , for  $1 \text{ mol l}^{-1}$  solution at  $25^\circ \text{C}$  [17]. Lithium was deposited from  $\text{LiClO}_4$  ( $1 \text{ mol l}^{-1}$ )-PC solution at current densities of up to  $10 \text{ mA cm}^{-2}$ , without any sign of gas evolution or side reaction. The Li deposit was grey and formed an alloy with the Pt substrate. The Li-Pt alloy was stable toward air and water. Immersing the deposit in water results in a violent reaction of the free lithium deposit, while the Li-Pt alloy remained stable. The platinum surface turned permanently grey and rough, and there was no way to regain the bright appearance of platinum. Lithium metal was found to alloy with other metals, including noble metals [18]. Alloying was not obtained when lithium was deposited on nickel or stainless steel cathodes. Prolonged deposition of lithium led to the formation of lithium trees.

**3.1.4.  $\text{LiPF}_6$ .** Lithium was deposited from  $0.5 \text{ mol l}^{-1}$   $\text{LiPF}_6$  solution in PC. The current densities were in the range of  $1\text{--}10 \text{ mA cm}^{-2}$  at relatively low applied potentials. The Li deposit was grey and very similar to the one obtained from  $\text{LiClO}_4$  solution. The solubility of  $\text{LiPF}_6$  is approximately  $0.55\text{--}0.76 \text{ mol l}^{-1}$  [19, 20].

**3.1.5.  $\text{LiBF}_4$ .** Lithium was deposited from a saturated solution of  $\text{LiBF}_4$  in PC. The concentration was below  $0.5 \text{ mol l}^{-1}$ . The solubility is  $0.42 \text{ mol l}^{-1}$ . A grey deposit was obtained at  $1 \text{ mA cm}^{-2}$  and moderate applied potentials.

**3.1.6.  $\text{LiAlCl}_4$ .** Lithium was deposited from a 1 : 1 mixture of  $\text{LiCl}$  and  $\text{AlCl}_3$  solution in PC. The solubility of  $\text{LiCl}$  in pure PC is low; however, in the presence of  $\text{AlCl}_3$ , which is highly soluble, the solubility of  $\text{LiCl}$  increases up to a 1 : 1 ratio. The anhydrous  $\text{AlCl}_3$  used contains 0.02% iron as its main impurity.  $\text{FeCl}_3$  cannot be removed by sublimation; its presence in the solution in very minor quantity probably does not interfere with the deposition of the alkali metal. Moreover, it should be expected that a  $\text{FeCl}_4^-$  complex is formed in a similar way to the formation of  $\text{AlCl}_4^-$ . Addition of  $\text{AlCl}_3$  to PC results in a violent reaction, accompanied by strong heating and darkening of the solution. This can be avoided by adding the  $\text{LiCl}$  first, then adding the  $\text{AlCl}_3$  extremely slowly while cooling the solution with a mixture of chloroform-carbon tetrachloride-dry  $\text{CO}_2$ . Solutions prepared in this way were almost colourless. Another successful method is to prepare the complex salt  $\text{LiAlCl}_4$  by heating a stoichiometric mixture of  $\text{LiCl}$  and  $\text{AlCl}_3$  at  $200^\circ \text{C}$  under a dry argon atmosphere. Addition of  $\text{LiAlCl}_4$  prepared in this way, to PC, resulted in no heating at all. Despite the superior solutions obtained by this method, in most experiments the solutions were prepared by the careful addition of  $\text{AlCl}_3$  to the  $\text{LiCl}$ -PC mixture. The second method was inconvenient because of the strong sublimation of  $\text{AlCl}_3$  at high temperature. Kinetic and thermodynamic measurements of  $\text{LiCl}$  and  $\text{AlCl}_3$ -PC solution are reported by Jörn  and Tobias elsewhere [23, 26].

In conclusion, perchlorate and aluminum tetrachloride solutions were found to be promising for the deposition of lithium and sodium.  $\text{LiPF}_6$  and  $\text{LiBF}_4$  are suitable for lithium deposition; however, their solubilities in PC are somewhat lower.

### 3.2. Sodium

$\text{NaCl}$  and  $\text{NaBr}$  are practically insoluble in PC and therefore not suitable for electrodeposition purposes.  $\text{NaClO}_4$ ,  $\text{NaPF}_6$ , and  $\text{NaAlCl}_4$  are quite soluble and therefore were tested. Furthermore, polarization and cyclic polarization experiments were performed for these electrolytes.

**3.2.1.  $\text{NaClO}_4$ .** The solubility of  $\text{NaClO}_4$  in PC is  $> 2 \text{ mol l}^{-1}$  [24]. Sodium was deposited from  $1 \text{ mol l}^{-1}$   $\text{NaClO}_4$  solution at a current density of

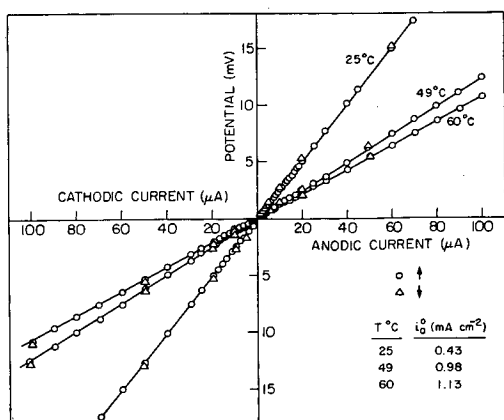


Fig. 2. Polarization of Na(s)/NaClO<sub>4</sub> (1 mol l<sup>-1</sup>), PC.

10 mA cm<sup>-2</sup> without any visible sign of gas evolution or side reaction. The deposit was grey, quite thick (0.5 mm) and did not form an alloy with the Pt cathode. The bias potentials between the Na electrodes were below 0.5 mV, even after a series of polarization experiments.

Fig. 2 shows the polarizations of sodium in NaClO<sub>4</sub> (1 mol l<sup>-1</sup>) solution at 25, 49 and 60°C after the overpotentials were corrected for ohmic drop, using a current interrupter technique. The exchange current densities were calculated from the slopes of the lines and from the area of the electrode. The exchange current densities are 0.43, 0.98 and 1.13 mA cm<sup>-2</sup> at 25, 49, and 60°C respectively, in good agreement with a value of 0.21 mA cm<sup>-2</sup> at 19°C, reported by Meibuhr [25]. The enthalpy of activation at zero polarization,  $\Delta H_0^*$  = 6.0 Kcal mol<sup>-1</sup>, was calculated from the slope of  $\ln i_0$  versus  $1/T$ ; Meibuhr obtained a value of 14.6 Kcal mol<sup>-1</sup>. The present result seems more reasonable for a soft metal like sodium, and is in better agreement with  $\Delta H_0^*$  = 8.5 Kcal mol<sup>-1</sup> obtained for Li/LiClO<sub>4</sub> in PC [21]. The micropolarization of NaClO<sub>4</sub> in PC reported by Meibuhr was performed only in the anodic direction, whereas in the present work the cathodic portion is included. The identical slopes in both cathodic and anodic directions indicate high reversibility of the dissolution-deposition process.

**3.2.2. NaPF<sub>6</sub>.** The solubility of NaPF<sub>6</sub> in PC is 0.86 mol l<sup>-1</sup> [19]. Sodium has been deposited from 0.5 mol l<sup>-1</sup> solution of NaPF<sub>6</sub> in PC at current densities of 1–10 mA cm<sup>-2</sup>. The deposit was

grey and there was no visible evidence of side reaction or gas evolution at the cathode. The potential between sodium electrodeposited on the Pt electrode and the reference sodium electrode was below 1.15 mV.

Polarization experiments were conducted to investigate the kinetic behaviour of metallic sodium and sodium amalgam in NaPF<sub>6</sub> (0.5 mol l<sup>-1</sup>) solution in PC. The polarization experiments were performed in a six-compartment cell in which two sodium, two sodium amalgam and two Pt electrodes were placed [23]. The sodium amalgam concentrations were 0.286 and 0.351 wt %, and the average potential differences between these electrodes and the sodium electrodes at 25°C were 831.9 and 734.7 mV, respectively. Constant current was applied in both cathodic and anodic directions between the sodium and the amalgam electrodes, and the two remaining electrodes served as reference electrodes. The measured overpotentials were corrected for ohmic drop by the current interrupter pulse technique, and the calculated exchange current densities are 18.1 and 10.6  $\mu$ A cm<sup>-2</sup> for sodium and sodium amalgam, respectively.

**3.2.3. NaBF<sub>4</sub>.** Despite the low solubility of NaBF<sub>4</sub> in PC, 0.093 mol l<sup>-1</sup> [19], sodium was successfully deposited from a saturated solution at 1 mA cm<sup>-2</sup> and moderately high applied potential. The deposit was grey. The limiting current was undoubtedly exceeded, as evidenced by gas evolution observed along with sodium deposition.

**3.2.4. NaAlCl<sub>4</sub>.** The solubility of NaCl in 1 mol kg<sup>-1</sup> AlCl<sub>3</sub> solution in PC was found to be around 0.5 mol kg<sup>-1</sup>. Sodium was electrodeposited from NaCl (0.5 mol kg<sup>-1</sup>)-AlCl<sub>3</sub> (1 mol kg<sup>-1</sup>) in PC at current densities 1–10 mA cm<sup>-2</sup> without any sign of gas evolution or side reaction. The deposit was grey and heavy. Further thermodynamic, kinetic and conductance measurements have been reported elsewhere [10, 26, 23].

### 3.3. Potassium

Potassium was found to be very reactive toward PC solutions. The surface of a bright potassium electrode turned purple within a few minutes in moderately dry PC (around 50 ppm H<sub>2</sub>O). The

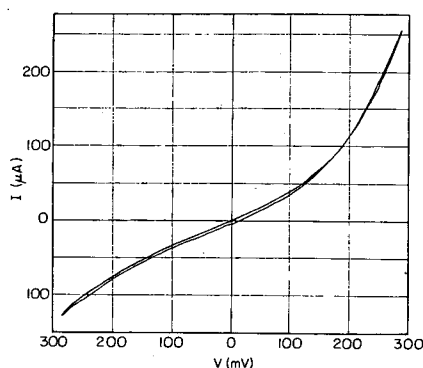


Fig. 3. Cyclic polarization for K in  $\text{KAlCl}_4$  ( $0.5 \text{ mol l}^{-1}$ )-PC. Reference electrode: K; sweep rate:  $1.2 \text{ mV s}^{-1}$ ; temperature:  $43^\circ\text{C}$ .

stability of potassium increased significantly after the PC was treated with molecular sieves (Linde 4A). The molecular sieves, approximately 5% volume, were added to PC and the mixture stirred for several hours.

Due to the low solubility of KCl ( $3.52 \times 10^{-4} \text{ mol l}^{-1}$  [7], KBr ( $6 \times 10^{-3} \text{ mol l}^{-1}$  [6],  $\text{KBF}_4$  ( $0.012 \text{ mol l}^{-1}$ ) [6] and  $\text{KClO}_4$  in PC, the only practical possibilities were found to be  $\text{KPF}_6$  and  $\text{KAlCl}_4$ . Nevertheless, potassium was electro-deposited from its perchlorate and tetrafluoroborate as well, at the very low current,  $0.1 \text{ mA cm}^{-2}$ , and high applied potentials.

**3.3.1.  $\text{KPF}_6$ .** The solubility of  $\text{KPF}_6$  in PC is  $1.2 \text{ mol l}^{-1}$  [27]. Potassium was deposited from  $\text{KPF}_6$  ( $0.5 \text{ mol l}^{-1}$ ) solution at current densities up to  $10 \text{ mA cm}^{-2}$ . Potassium wire served as the anode; normal anodic dissolution was observed, while the deposit on the platinum cathode was grey and loose. The bias potential between the deposited potassium and the potassium anode, after the deposition was completed, was less than 20 mV.

**3.3.2.  $\text{KAlCl}_4$ .** Potassium was electrodeposited from 1 : 1 KCl- $\text{AlCl}_3$  ( $0.5 \text{ mol l}^{-1}$ ) in PC. The electrodeposition was performed in a six-compartment cell, where potassium wire served as an anode and platinum foil as a cathode. The nature of the deposit was checked by measuring the bias potentials between the deposited potassium, the reference potassium electrode, and two separate potassium amalgam electrodes (0.451 wt %). The potentials between the deposited potassium and the

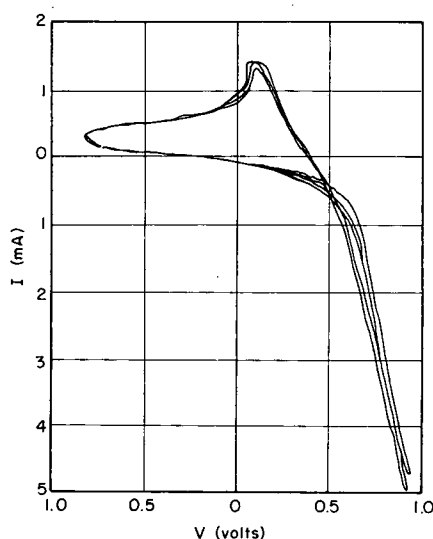


Fig. 4. Cyclic polarization for Pt in  $\text{KAlCl}_4$  ( $0.5 \text{ mol l}^{-1}$ )-PC. Reference electrode: K(Hg); sweep rate:  $0.4 \text{ mV s}^{-1}$ ; temperature:  $25^\circ\text{C}$ .

reference potassium electrode were always below 20 mV immediately after the deposition. However, within a few hours after the current was turned off, the potential difference increased substantially; it was observed that the potassium deposit became loose and the Pt substrate was exposed.

The potential differences between the potassium wire and the K(Hg) electrodes were measured and recorded over a period of four days at different temperatures. Although the electrodes were subjected to polarization runs during this period, the open circuit potentials remained constant within  $\pm 10 \text{ mV}$ . The potential difference between metallic potassium and potassium amalgam (0.451 wt %) in  $0.5 \text{ mol l}^{-1}$   $\text{KAlCl}_4$  solution in PC at  $25^\circ\text{C}$  was 1.007 V. Kinetic and thermodynamic measurements are reported elsewhere [23, 26].

The stability and the reversibility of potassium and its amalgam in  $\text{KAlCl}_4$  solution in PC were tested by a linear cyclic polarization technique. Fig. 3 shows two cyclic polarizations for K in  $\text{KAlCl}_4$  ( $0.5 \text{ mol l}^{-1}$ ) PC solution, at  $43^\circ\text{C}$ . At the sweep rate of  $1.2 \text{ mV s}^{-1}$  no hysteresis was observed after a complete cycle. The behaviour of a clean platinum electrode in the same  $\text{KAlCl}_4$  ( $0.5 \text{ mol l}^{-1}$ ) PC solution was investigated and is presented in Fig. 4. Three complete cycles were recorded, and negligible anodic current can be observed when the potential is swept in the



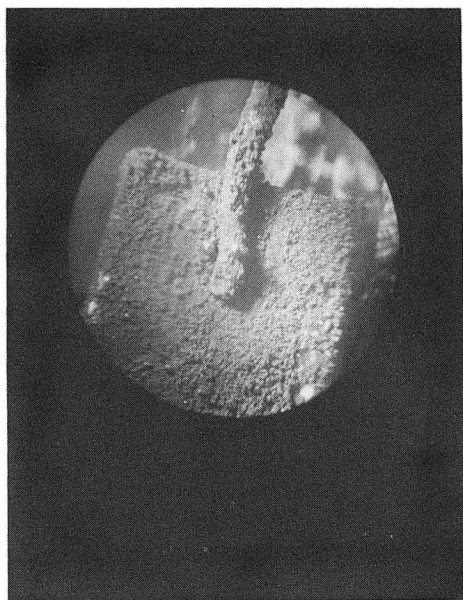


Fig. 5. Cesium deposit on a platinum cathode, from  $\text{CsAlCl}_4$  ( $0.25 \text{ mol l}^{-1}$ ) PC solution. Current density:  $1 \text{ mA cm}^{-2}$ ; temperature:  $25^\circ\text{C}$ .

cathodic direction. The cathodic behaviour is linear; however, cycling back in the anodic direction, anodic current peaks can be observed, caused by the re-dissolution of the deposited potassium from the platinum surface. The small anodic current on the clean Pt demonstrates the stability of the solvent in the far cathodic potential range.

### 3.4. Rubidium

Due to the low solubility of most of the common Rb salts in PC, the only practical possibility for electrodeposition studies was offered by the combination between  $\text{RbCl}$  and  $\text{AlCl}_3$ .

Rubidium was deposited from a carefully dried 1 : 1  $\text{RbCl-AlCl}_3$  ( $1 \text{ mol l}^{-1}$ ) solution in PC at currents up to  $10 \text{ mA cm}^{-2}$ . The electrodeposition was conducted in a six-compartment cell, where metallic Rb, Rb amalgam ( $0.2306 \text{ wt } \%$ ) and a platinum electrode served as the anode, the reference electrode and the cathode, respectively. The potential between the metallic rubidium and the amalgam was recorded over a period of four days. The average potential was  $1.076 \text{ V}$  at  $25^\circ\text{C}$ , in good agreement with the value of  $1.0745 \text{ V}$  measured by G. N. Lewis and W. L. Argo [28] in ethylamine. The composition of the amalgam

matched exactly the amalgam composition used by Lewis and Argo.

The potential between freshly electrodeposited rubidium and the bulk metal was below  $25 \text{ mV}$  immediately after the electrodeposition. This bias potential increased significantly after a few hours of standing, when the deposit became loose and the platinum substrate was exposed.

Cyclic polarization of Rb and  $\text{Rb(Hg)}$  in  $\text{RbAlCl}_4$  ( $0.5 \text{ mol l}^{-1}$ ) shows similar behaviour to the behaviour of potassium. Kinetic and emf data are presented elsewhere [23, 26].

### 3.5. Cesium

Of the common cesium salts tried, only  $\text{CsAlCl}_4$  ( $\text{CsCl} + \text{AlCl}_3$ ) gave good solubility and a good deposit in PC. Cesium was deposited from  $\text{CsClO}_4$  solution in PC, but because of the low solubility the current was very low and was accompanied by high applied potential. Gas evolution was observed during this experiment.

$\text{CsCl}$  was found to be soluble in  $\text{AlCl}_3$  solution in PC, while  $\text{CsBr}$  was found to be insoluble in the same  $\text{AlCl}_3$  solution. Cesium was deposited from carefully dried  $\text{CsAlCl}_4$  ( $0.25 \text{ mol l}^{-1}$ ) solution in PC. The cesium deposit on a platinum foil electrode is shown in Fig. 5. The deposit was silvery grey and globules can be observed on the surface. The deposit melted at  $29^\circ\text{C}$ , slightly above the melting point of Cs ( $28.4^\circ\text{C}$ ).

The experiment was conducted in a six-compartment cell, where two cesium cup electrodes, two cesium amalgam ( $0.302 \text{ wt } \%$ ) cup electrodes and two platinum electrodes served respectively as anode, reference electrode and cathode. The potential between the deposited cesium and the metallic cesium was below  $20 \text{ mV}$ , and changed significantly after a few hours of standing, due to the re-exposure of the platinum substrate. The cesium amalgam composition did not match exactly the composition of the amalgam used by Bent *et al.* [29] (the only source of data for cesium). However, the present value of  $1.107 \pm 0.010 \text{ V}$  for  $0.302 \text{ wt } \%$  Cs is in the right direction when compared to the  $1.119 \text{ V}$  value obtained by Bent *et al.* [29] for a  $0.1875 \text{ wt } \%$  cesium amalgam. These two values represent the only emf data for cesium available at room temperature.

Micropolarizations of cesium in  $\text{CsAlCl}_4$  ( $0.25$

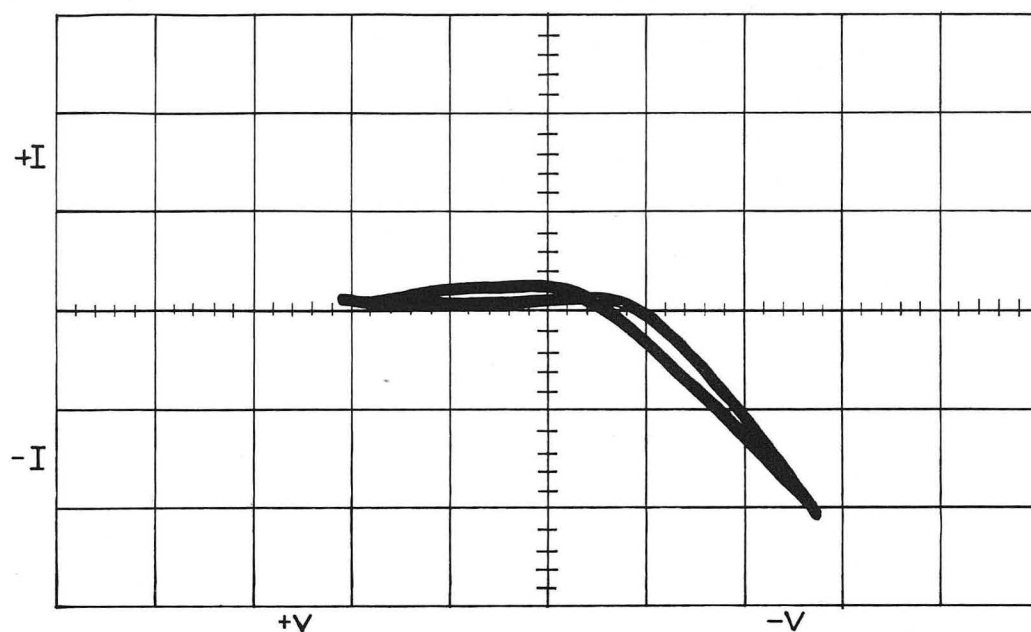


Fig. 6. Cyclic polarization of a clean anodized Pt electrode in  $\text{CsAlCl}_4$  ( $0.25 \text{ mol l}^{-1}$ )-PC. Sweep rate:  $0.25 \text{ V s}^{-1}$ ; reference electrode: Cs;  $0.8 \text{ V cm}^{-1}$ ;  $0.25 \text{ mA cm}^{-1}$ .

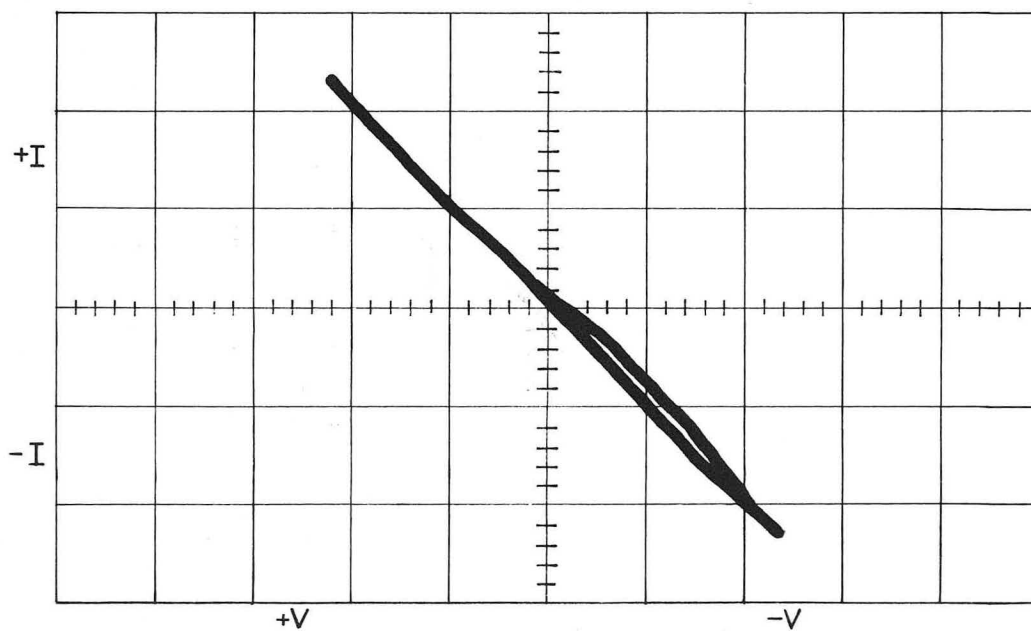


Fig. 7. Cyclic polarization of a Cs deposit on a Pt electrode in  $\text{CsAlCl}_4$  ( $0.25 \text{ mol l}^{-1}$ )-PC. Sweep rate:  $0.25 \text{ V s}^{-1}$ ; reference electrode: Cs;  $0.8 \text{ V cm}^{-1}$ ;  $0.25 \text{ mA cm}^{-1}$ .

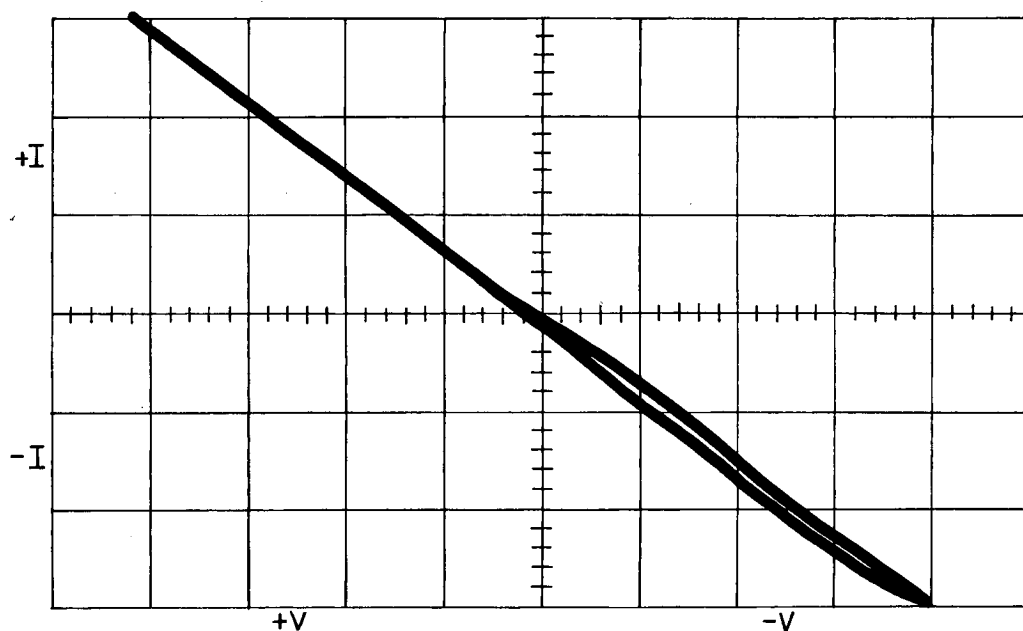


Fig. 8. Cyclic polarization of a pure Cs electrode in  $\text{CsAlCl}_4$  ( $0.25 \text{ mol l}^{-1}$ )-PC. Sweep rate:  $0.25 \text{ V s}^{-1}$ ;  $0.5 \text{ V cm}^{-1}$ ;  $0.5 \text{ mA cm}^{-1}$ .

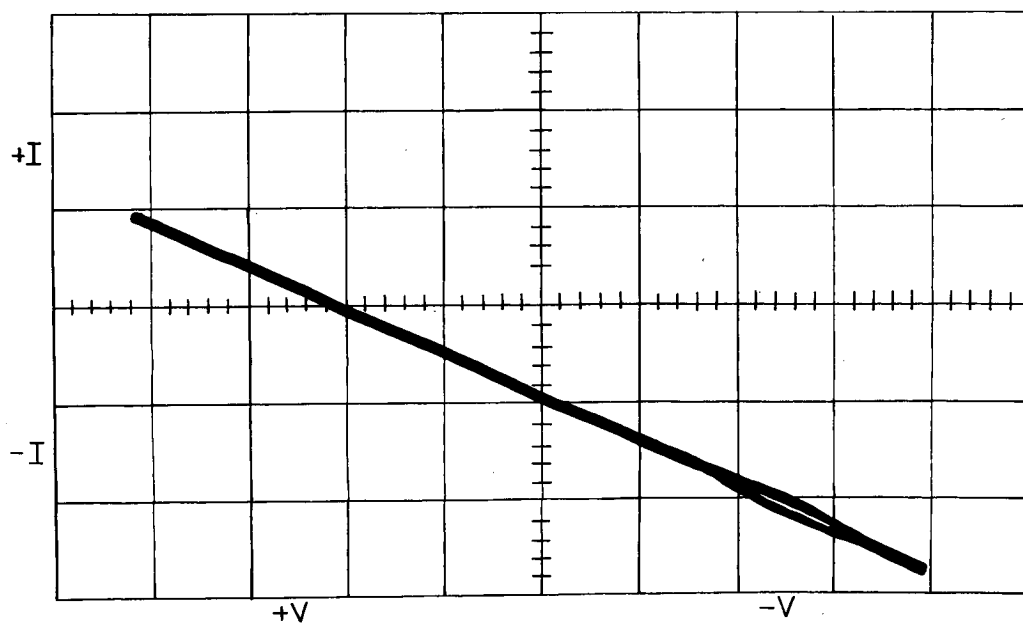


Fig. 9. Cyclic polarization of a Cs(Hg) electrode, 0.302 wt % in  $\text{CsAlCl}_4$  ( $0.25 \text{ mol l}^{-1}$ )-PC. Sweep rate:  $0.25 \text{ V s}^{-1}$ ; reference electrode: Cs;  $0.5 \text{ V cm}^{-1}$ ;  $0.5 \text{ mA cm}^{-1}$ .

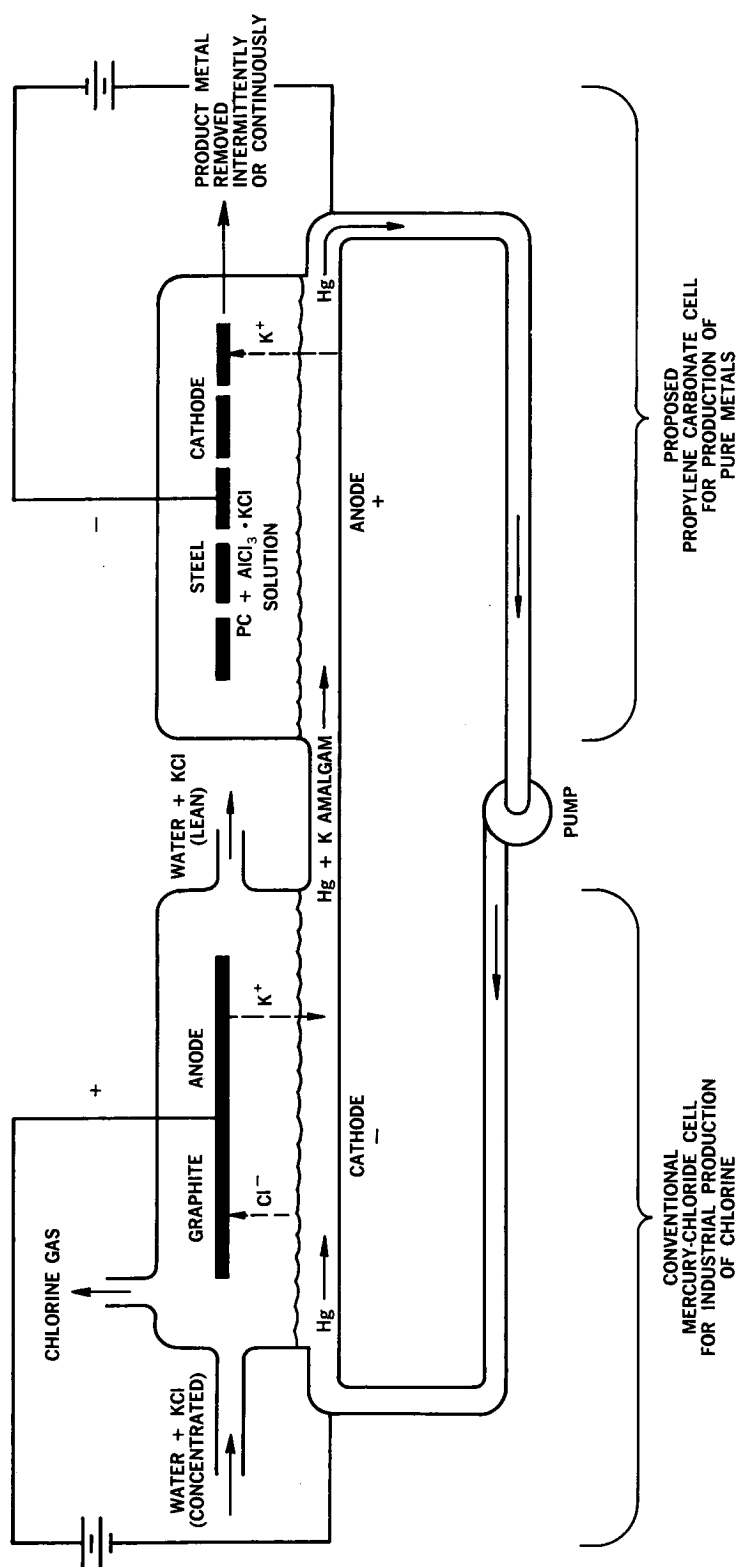


Fig. 10. Schematic diagram of the proposed electrowinning process. *Electrowinning*. Alkali metal-potassium (K) is amalgamated with mercury (Hg) from a water solution of the alkali metal salt (KCl). Chlorine is given off and collected. *Electrorefining*. In a solution of propylene carbonate (PC) and selected salts, the alkali metal (K) leaves the amalgam and is deposited in pure form on the cathode, from which it can be collected.

$\text{mol l}^{-1}$ ) were performed at four different temperatures [23]; the exchange current densities  $i^0$  were calculated from the slopes and were plotted versus  $1/T$  (see Figs. 8 and 9 in reference [23]). The enthalpy of activation at zero polarization was calculated from the slope to be  $\Delta H_0^* = 10.4 \text{ Kcal mol}^{-1}$ . The exchange current at  $23.5^\circ\text{C}$  was lower than expected, probably because at  $23.5^\circ\text{C}$  Cs is a solid, while the other three temperatures were above the melting point of cesium,  $28.4^\circ\text{C}$ . Complete kinetic and emf data for Cs are presented elsewhere [23, 26].

In addition to the galvanostatic deposition experiments, the deposition-dissolution of cesium on a platinum electrode was investigated by a linear cyclic polarization technique.

The oscillograms in Figs. 6–9 show the behaviour of platinum, deposited cesium, metallic cesium and cesium amalgam in  $\text{CsAlCl}_4$  ( $0.25 \text{ mol l}^{-1}$ ) in PC at  $25^\circ\text{C}$ . The scanning rate was  $0.25 \text{ V s}^{-1}$ . Fig. 6 shows the behaviour of a clean platinum electrode. The anodic current is negligible because of the absence of active metal on the electrode. The cathodic current increases linearly with the scanning potential. The anodic branch following a single cathodic cycle shows a small current due to the redissolution of the deposited cesium; scanning started from the far anodic side. Fig. 7 shows the behaviour of electrodeposited cesium on a platinum substrate after 4 h of cathodic deposition at  $1 \text{ mA cm}^{-2}$ . The behaviour is similar to the behaviour of pure metallic cesium in the same solution shown in Fig. 8. Fig. 9 shows the behaviour of cesium amalgam (0.2306 wt %) in the same  $\text{CsAlCl}_4$  ( $0.25 \text{ mol l}^{-1}$ ) PC solution.

It is difficult to see why no stripping peak is observed for Cs in Fig. 6, while for potassium in Fig. 4 a stripping peak is observed. It is possible that some impurities formed codeposits causing peeling of the deposit from the substrate. The peeling of the deposit idea is supported by the time dependent bias potential of the Cs deposit.

#### 4. Conclusions

The results of the present work have established the feasibility of the electrodeposition of the alkali metals from their solutions in propylene carbonate at ambient temperature. The following conclusions were obtained:

- (1) Li, Na, K, Rb and Cs can be reduced from various salt solutions in PC, with high efficiency. Among the salts employed, best results were obtained from  $\text{ClO}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{BF}_4^-$  and particularly from double salts involving the chloride of the metal and  $\text{AlCl}_3$  in PC. From the latter, a typical composition of the electrolyte would involve  $1 \text{ mol kg}^{-1}$  alkali metal chloride in  $1 \text{ mol kg}^{-1}$   $\text{AlCl}_3$ -PC solution.
- (2) The alkali metals and the alkali metal amalgams demonstrate moderate to low exchange current densities in PC ( $0.01$ – $1.0 \text{ mA cm}^{-2}$ ).
- (3) The alkali metals can be anodically dissolved from and cathodically deposited into the metal electrode or its amalgam.
- (4) These favourable results led us to propose a new process for the electrorefining and separation of the alkali metals at ambient temperature [9]. It is proposed that the alkali metal amalgam, which is produced commercially in the chlorine-mercury cell by aqueous electrolysis, be transferred into a nonaqueous cell containing a solution of the alkali metal chloride in  $\text{AlCl}_3$ -PC; the alkali metal would then be anodically dissolved from the amalgam and re-deposited in a pure form at the metallic cathode. A schematic diagram of the proposed process for the case of potassium is shown in Fig. 10. The first step in this process is the same as the mercury-cell method commonly used to produce chlorine gas: a concentrated aqueous solution of potassium chloride is electrolyzed, chlorine gas is given off at the anode and potassium is deposited into the mercury cathode. Next, the potassium amalgam — instead of reacting with water to form hydroxide as in chlorine-caustic manufacture — flows into a propylene carbonate cell in which potassium is redissolved and deposited in pure form on an inert cathode. The main products are therefore chlorine, as before, and metallic potassium instead of potassium hydroxide.

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## References

- [1] L. F. Audrieth and J. Kleinberg, 'Non-Aqueous Solvents', John Wiley and Sons, New York (1953).
- [2] F. Walden, *Ber. dtsh. Chem. Ges.* **32** (1899) 2862.
- [3] P. Walden, 'Elektrochemie Nichtwasserigen', J.A. Barth, Leipzig (1924).
- [4] L. F. Audrieth and H. W. Nelson, *Chem. Rev.* **8** (1931) 335.
- [5] A. Brenner, Electrolysis of nonaqueous systems, 'Advances in Electrochemistry and Electrochemical Engineering', P. Delahay and C. W. Tobias, eds., Interscience, New York (1967) Vol. 5.
- [6] W. S. Harris, Thesis, UCRL 8381, University of California (1958).
- [7] R. Jasinski, Electrochemistry and application of propylene carbonate, 'Advances in Electrochemistry and Electrochemical Engineering', P. Delahay and C. W. Tobias, eds., Interscience, New York (1971) Vol. 8.
- [8] James N. Butler, Reference electrodes in aprotic organic solvents, 'Advances in Electrochemistry and Electrochemical Engineering', P. Delahay and C. W. Tobias, eds., Interscience, New York (1970) Vol. 7.
- [9] C. W. Tobias and J. Jorné, Method of Production of the Alkali Metals and their Alloys, U.S. Patent 3,791,945 (Feb. 12, 1974).
- [10] J. Jorné, Dissertation, LBL 1111, University of California, Berkeley (1972).
- [11] F. G. K. Baucke, D. Landolt and C. W. Tobias, *Rev. Sci. Instr.* **39** (1968) 1753.
- [12] L. Hsueh, M. S. Thesis, UCRL 16607, University of California, Berkeley (1966).
- [13] J. Newman, *J. Electrochem. Soc.* **113** (1966) 501.
- [14] J. N. Butler, D. R. Cogley and J. C. Synnott, *J. Phys. Chem.* **73** (1969) 4026.
- [15] R. Fuoss and E. Hirsch, *J. Am. Chem. Soc.* **82** (1968) 1013.
- [16] R. Keller, et al., Fourth Quarterly Report, Contract NAS 3-8521, (July 1967).
- [17] *Idem*, Final Report, Contract NAS 3-8521 (Dec. 1969).
- [18] A. N. Dey, *J. Electrochem. Soc.* **118** (1971) 1547.
- [19] H. Bauman, Tech. Report APL-TD-R64-59 (May 1964).
- [20] A. Lyall, H. Seiger and J. Orshich, Tech. Report AFAPL-TR-68-71 (July 1968).
- [21] S. G. Meibuhr, *J. Electrochem. Soc.* **117** (1970) 56.
- [22] *Idem, ibid* **118** (1971) 1320.
- [23] J. Jorné and C. W. Tobias, *ibid* **121** (1974) 994.
- [24] Y. Wu and H. Friedman, *J. Am. Chem. Soc.* **70** (1966) 501, 2020.
- [25] S. G. Meibuhr, *J. Electrochem. Soc.* **118** (1971) 709.
- [26] J. Jorné and C. W. Tobias, *ibid* **122** (1975) 624.
- [27] W. Eliot, S. Hsu and W. Towle, Proc. Annual, Power Sources Conf. **18** (1964) 82; Final Report, Contract NAS 3-2790 (1964).
- [28] G. N. Lewis and W. L. Argo, *J. Am. Chem. Soc.* **37** (1915) 1983.
- [29] H. E. Bent, G. S. Forbes and A. F. Forziati, *ibid* **61** (1939) 709.

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